

Lithium-Bearing Mixed Polyanion (LBMP) Glasses as Cathode Materials

Project ID: ES184

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Oak Ridge National Laboratory

DOE Annual Merit Review

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Overview

Timeline

- Start date: June 22nd, 2012
- End date: Sept. 30th, 2015
- Percent complete: 51%

Budget

- Total funding: \$1.42M
 - DOE share: \$1.42M
- Funding received in FY2013: \$300K
- Funding received for FY2014: \$335K
(\$381K projected)

Barriers

- Higher energy densities (350 Wh/kg cell*)
 - Est. cathode energy densities up to >1000 Wh/kg
 - Excellent cycle life (PHEV 3-5K deep discharges*)
 - Rigid covalent structure & no irreversible phase changes
 - Cost (PHEV \$300/kWh*)
 - Commercial, non-exotic processing methods
- *VT Program Multi-Year Plan values

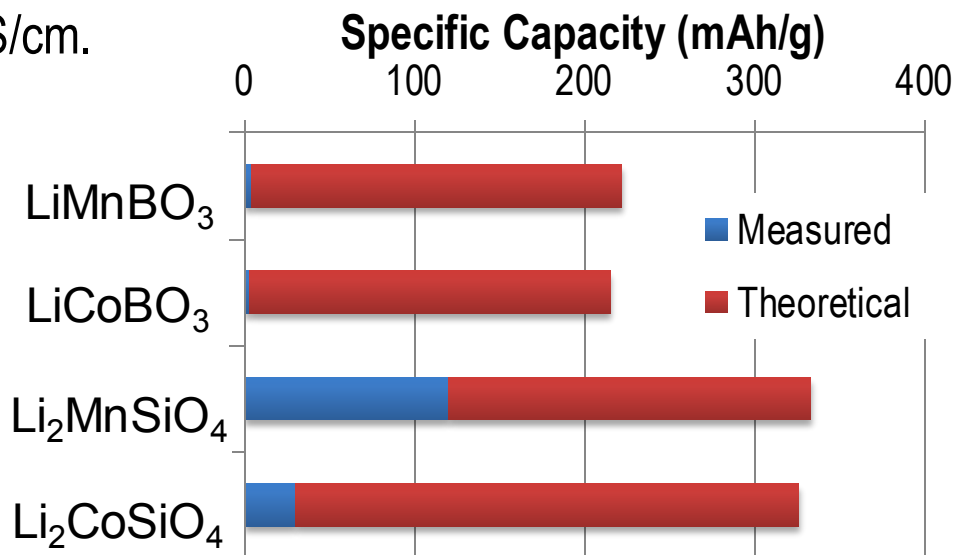
Partners

- Dr. Kyler Carroll (MIT): x-ray absorption spectroscopy of glass cathodes at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory
- Dr. Chris Wolverton (Northwestern): computational modeling of glass cathode discharge voltages using the Open Quantum Materials Database (OQMD)

Many crystalline polyanion cathodes have unrealized theoretical performance

Relevance

- Several highly promising polyanionic crystalline cathodes have failed due to poor electrical conductivity or irreversible phase transformations.
- The electrical conductivities of crystalline polyanion materials are very low.
 - At $\sim 10^{-9}$ - 10^{-10} S/cm, LiFePO_4 has a high conductivity for a polyanion material and has been the most successful as a cathode by far.
 - Electrical conductivities are often $\sim 10^{-12}$ S/cm.
- Multi-valent transitions in crystalline polyanion cathodes have not been significantly realized due to irreversible phase transformations that occur during battery testing.



1. Legagneur V, et al., 2001.
2. Domiko R, et al., 2007.
3. Lyness C, et al., 2007.

Polyanion glasses could succeed where crystalline cathode materials have failed

Relevance

- Mixed polyanion glasses can be designed to overcome the key shortcomings of crystalline polyanion cathode materials.
- Mixed polyanion glasses can have electrical conductivities orders of magnitude higher than similar polyanionic crystalline materials.
- During lithium cycling, glasses will not undergo irreversible phase transformations like crystalline materials.

Mixed polyanion glass cathodes offer the potential of achieving the excellent theoretical specific energies of promising crystalline framework materials.

Material	Electrical conductivity
Lithium iron phosphate	$\sim 10^{-9}$ - 10^{-10} S/cm
Iron phosphate glass	$\sim 10^{-10}$ S/cm
Iron phosphate glass – 30% vanadate substituted	$\sim 10^{-8}$ S/cm
Iron phosphate glass – 50% vanadate substituted	$\sim 10^{-6}$ S/cm

1. Mogus-Milankovic M, et al., 2004.
2. Tanaka K, et al., 1990.
3. Shapaan M, et al., 2009.
4. Santic B, et al., 2001.

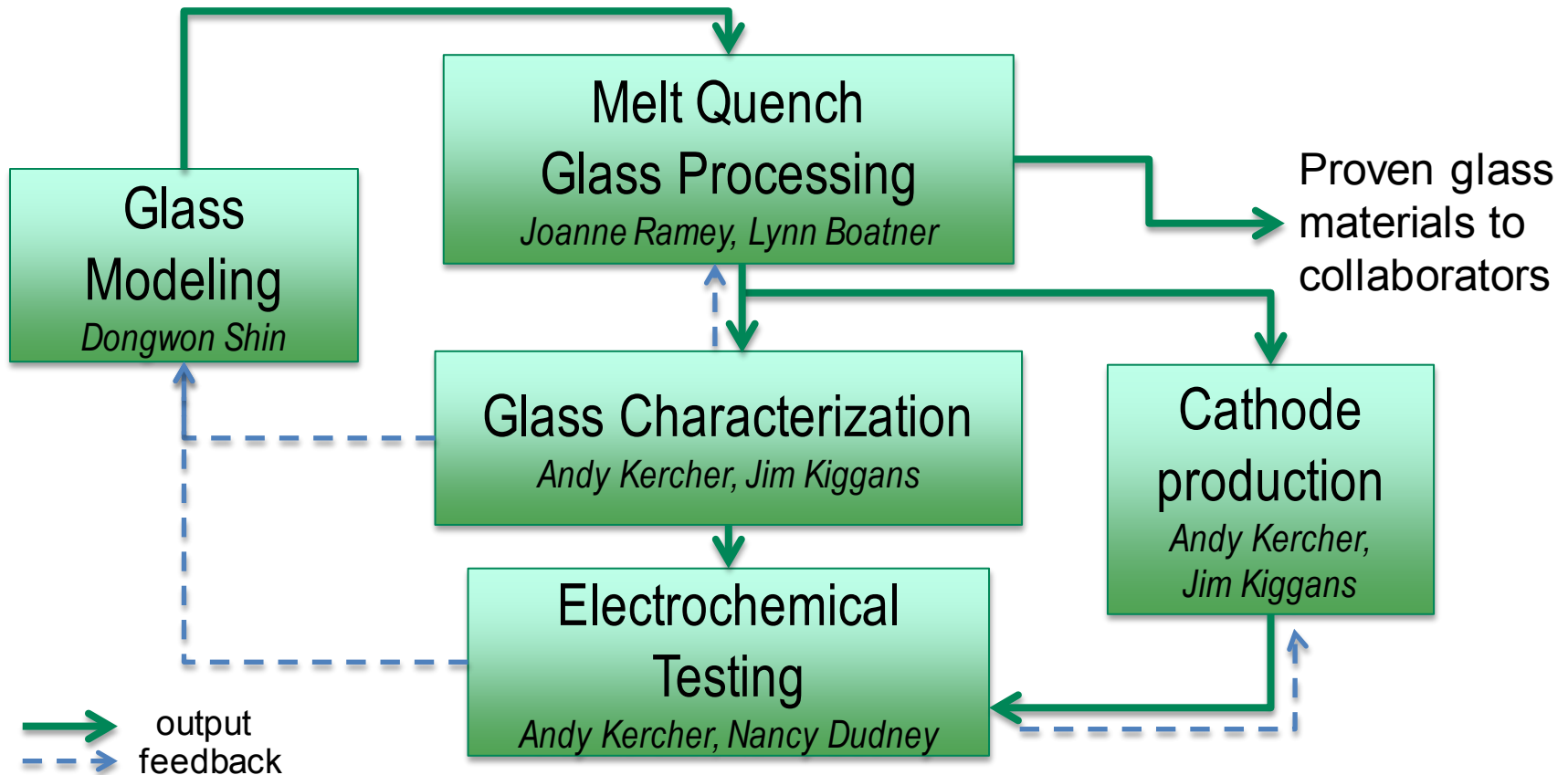
- Produce and electrochemically test mixed polyanion glasses containing a variety of transition metal cations that have the potential of achieving specific energies exceeding LiFePO_4
- Evaluate the cycling and rate performance of mixed polyanion glass cathodes
- Demonstrate the effect of reduced particle size on mixed polyanion glass cathode performance

- Jan. 2013: Setup CALPHAD database and perform initial simulation for one glass composition. *Completed on schedule*
- Sept. 2013: Synthesize, characterize, and perform electrochemical testing on at least 4 different glass compositions. *Completed on schedule*
- Sept. 2013: Create CALPHAD thermodynamic database and verify results with comparison to initial experimental glass compositions and electrochemical performance. *Completed on schedule*

- Dec. 2013: Synthesize, characterize, and perform electrochemical testing on a mixed polyanion glass that is theoretically capable of a multi-valent transition. *Completed on schedule*
- Mar. 2014: Demonstrate the effect of submicron particle size on the electrochemical performance of mixed polyanion glass cathodes. *Completed on schedule*
- June 2014: Measure the electrical conductivities of a series of mixed polyanion glasses as a function of polyanionic substitution.
- Sept. 2014: Synthesize, characterize, and perform electrical testing on at least 4 different glass cathode compositions with theoretical specific energies exceeding LiFePO_4 .

Program structure

Approach



- Target mixed polyanion glasses are chosen based on feedback from glass modeling, glass characterization, and battery testing results.

- Transition metals are chosen based on criteria such as:
 - Expected redox potential with given polyanion
 - Specific capacity
 - Possible high-voltage multi-valent transition (ex. Mn^{4+} to Mn^{2+}) within reasonable electrolyte voltage window
- Polyanion composition is based on:
 - Processability
 - Molecular weight
 - Amount of polyanion substitution to obtain desirable electrical conductivity ($>10^{-10}$ S/cm minimum)



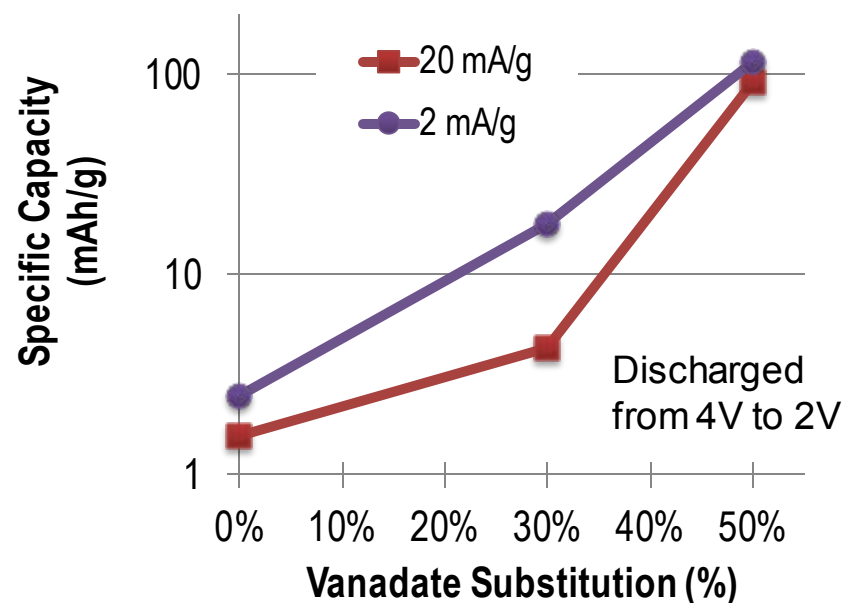
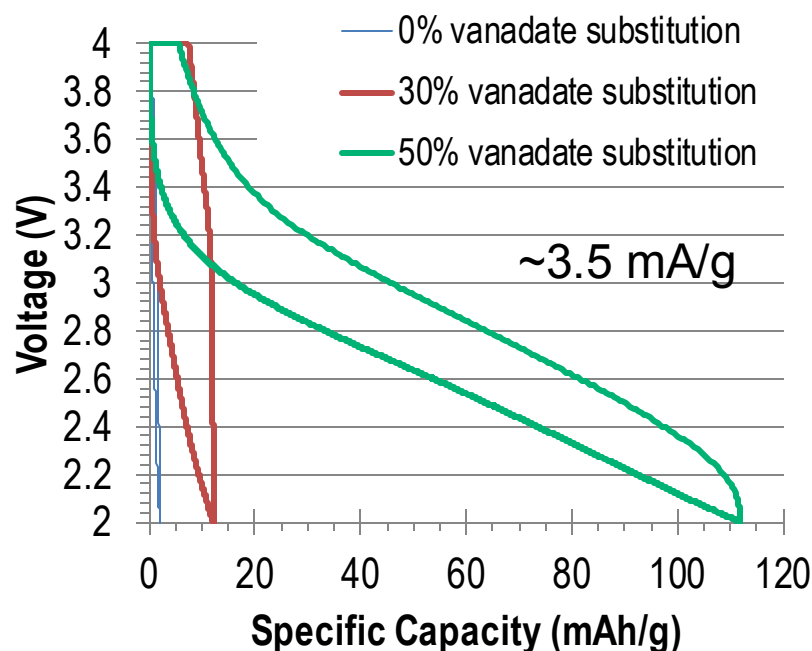
Iron phosphate glass for battery cathodes, as cast

Polyanion substitution improves electrochemical performance

Technical
Accomplishments

FY2013 key result

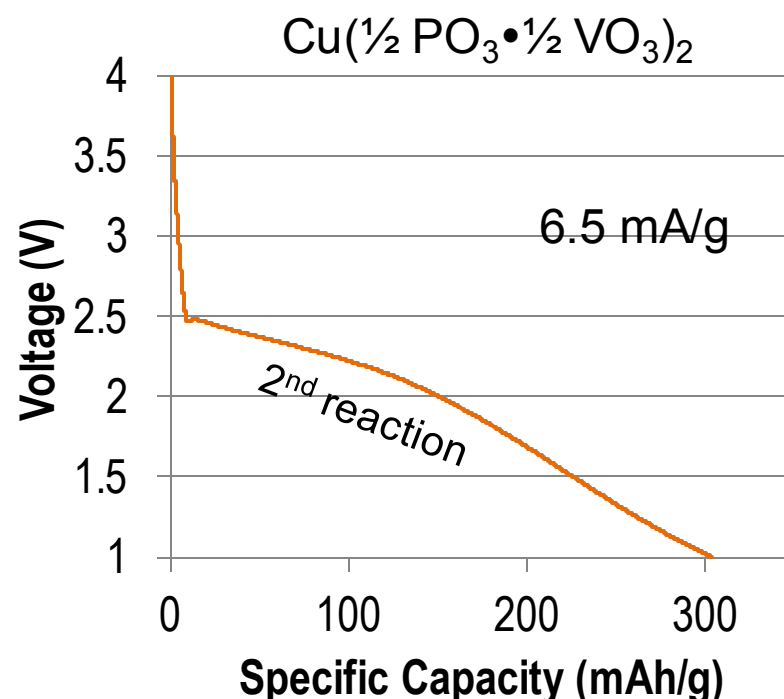
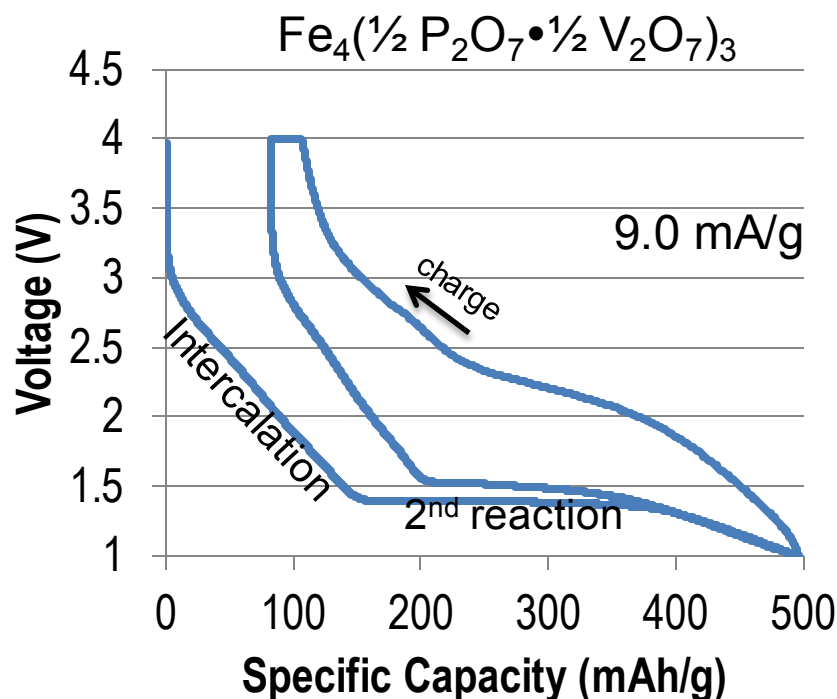
- In an iron pyrophosphate glass ($\text{Fe}_4(\text{P}_2\text{O}_7)_3$), polyanion substitution of the phosphate with vanadate dramatically improved the specific capacity and rate performance.
- Proof-of-concept: The rate performance and specific capacity of polyanion glass cathodes has been shown to improve with the substitution of vanadate polyanions.



Tape-cast cathode on aluminum current collector:
60% active material, 30% carbon, 10% PVDF

Unexpected high capacity 2nd electrochemical reaction

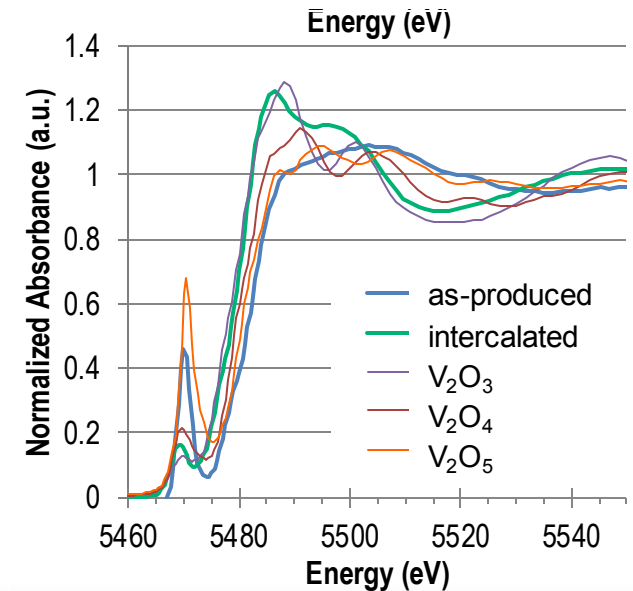
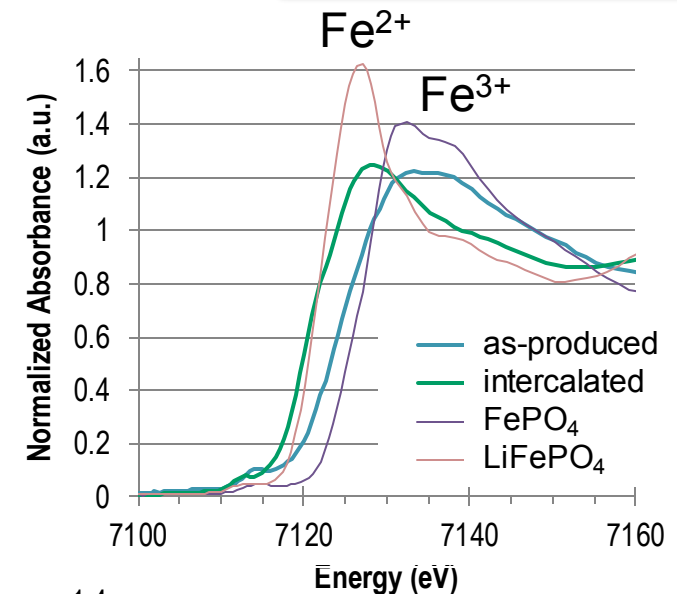
- Mixed polyanion glasses can undergo a high capacity intercalation reaction and/or a 2nd high capacity reaction.
- This unexpected 2nd reaction provides another possible route to designing high capacity glass cathode materials.



Tracking valence changes during intercalation reaction

Technical
Accomplishments

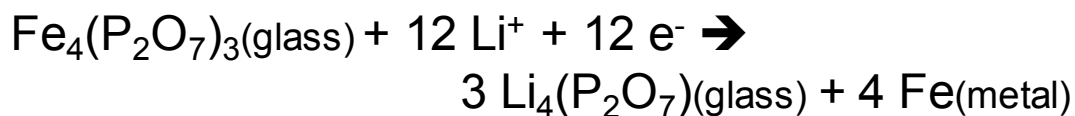
- X-ray absorption spectroscopy was used to determine the valence changes of Fe and V from the intercalation reactions of $\text{Fe}_4(\frac{1}{2} \text{P}_2\text{O}_7 \bullet \frac{1}{2} \text{V}_2\text{O}_7)_3$ glass.
- The main valence change is Fe^{3+} to Fe^{2+} , but vanadium valence changes also occur to a limited extent ($\text{V}^{5+/4+}$ to $\text{V}^{4+}/\text{V}^{3+}$)



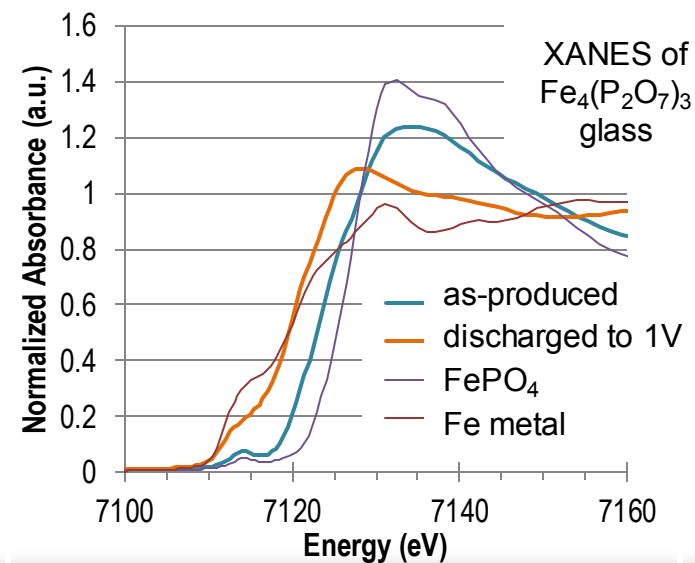
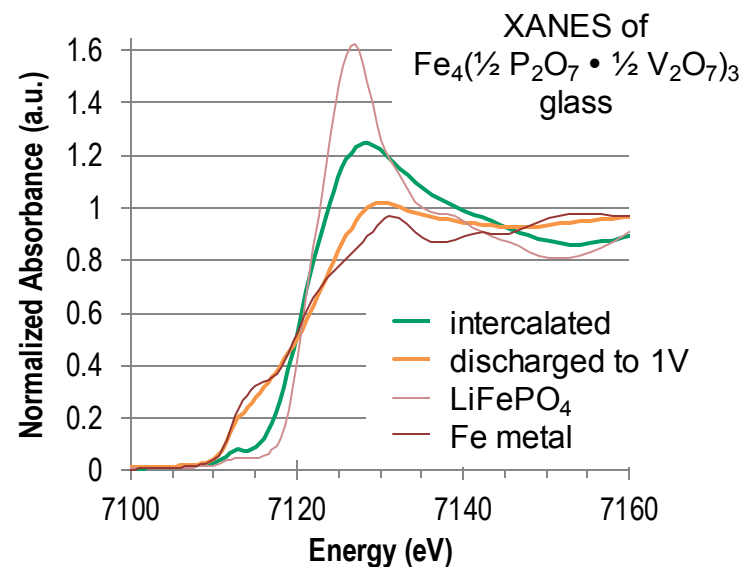
Strong evidence of glass-state conversion reaction

- For $\text{Fe}_4(\frac{1}{2} \text{P}_2\text{O}_7 \bullet \frac{1}{2} \text{V}_2\text{O}_7)_3$ and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ glass cathodes discharged to 1V, x-ray absorption spectroscopy showed that iron cations are reduced to iron metal.
- X-ray diffraction of discharged cathodes was consistent with presence of iron nanoparticles.

Example of proposed mechanism for “2nd reaction”:

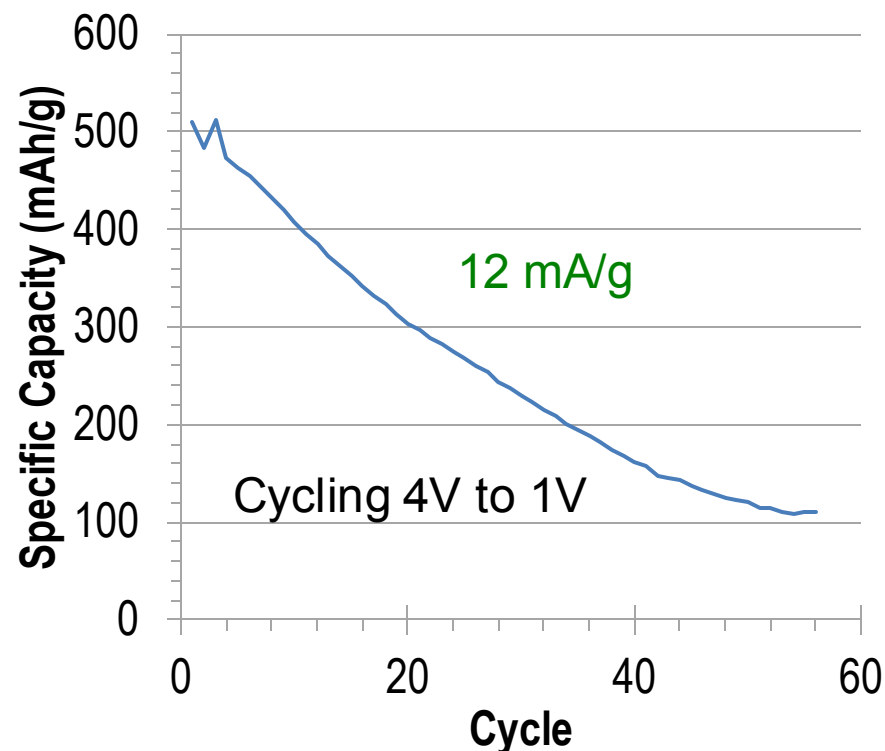
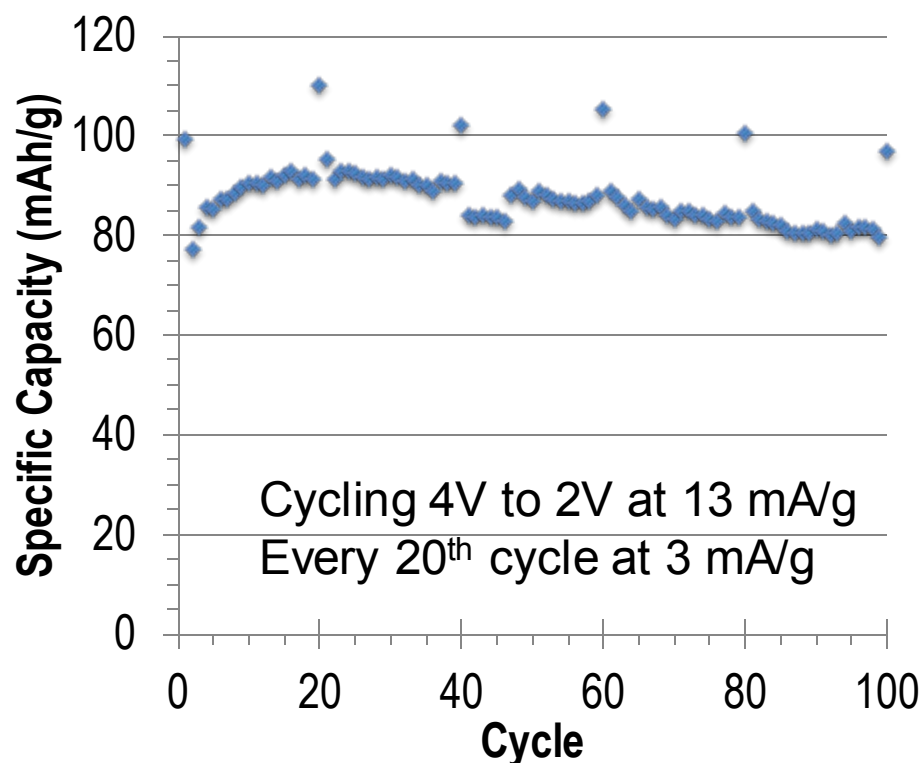


Glass-state conversion reaction



Glass cathode cycling behavior depends on electrochemical reaction type

Iron pyrophosphate glass with 50% vanadate substitution showed good cycleability in the intercalation reaction.



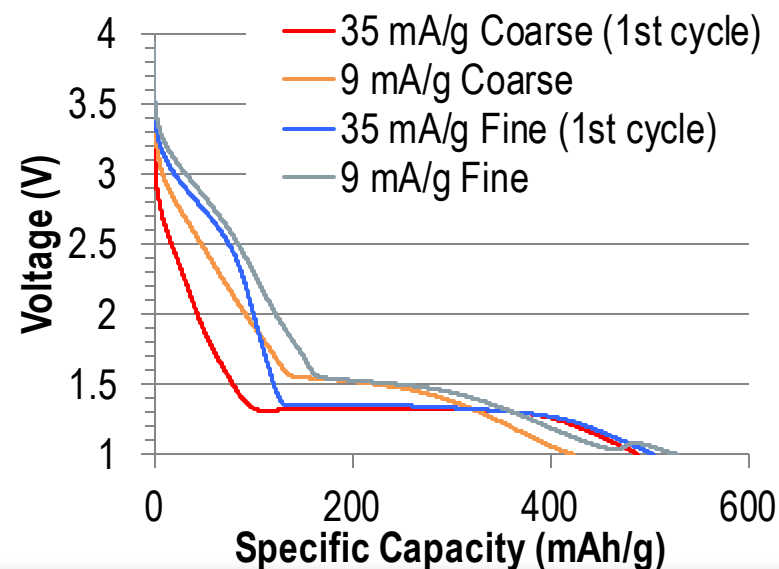
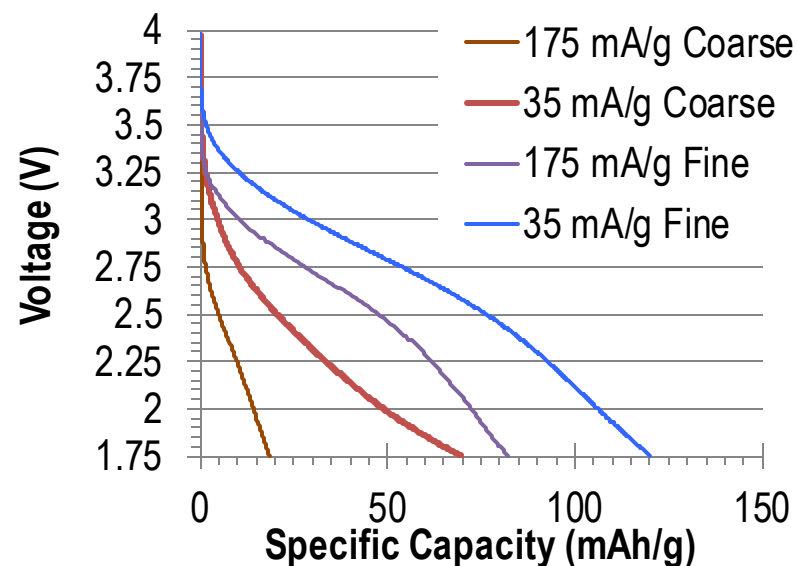
However, strong capacity fade was observed during cycling to include the glass-state conversion reaction.

Currently, the intercalation reaction cycles well, but the glass-state conversion reaction shows significant fade.


Particle size reduction improves rate performance and capacity

Technical Accomplishments

- $\text{Fe}_4(\frac{1}{2}\text{P}_2\text{O}_7 \bullet \frac{1}{2}\text{V}_2\text{O}_7)_3$ glass cathodes with two different particle sizes were discharged to 2V and to 1V.
 - Coarse: 4 m²/g, ~550 nm particle size
 - Fine: 25 m²/g, ~95 nm particle size
- For the intercalation reaction, the finer cathodes show dramatically improved capacity at higher discharge rates.
- Looking at both the intercalation and glass-state conversion reactions, finer glass cathodes can have higher specific energies.



Models predict glass-state conversion reaction voltages

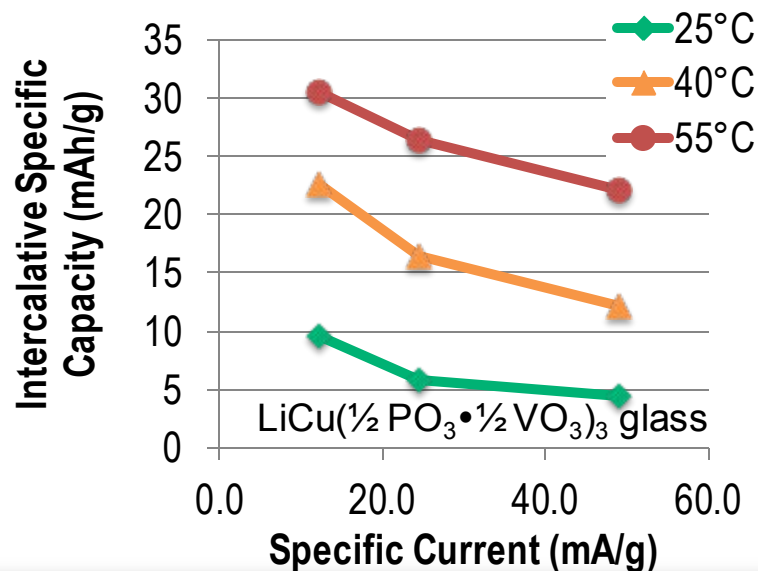
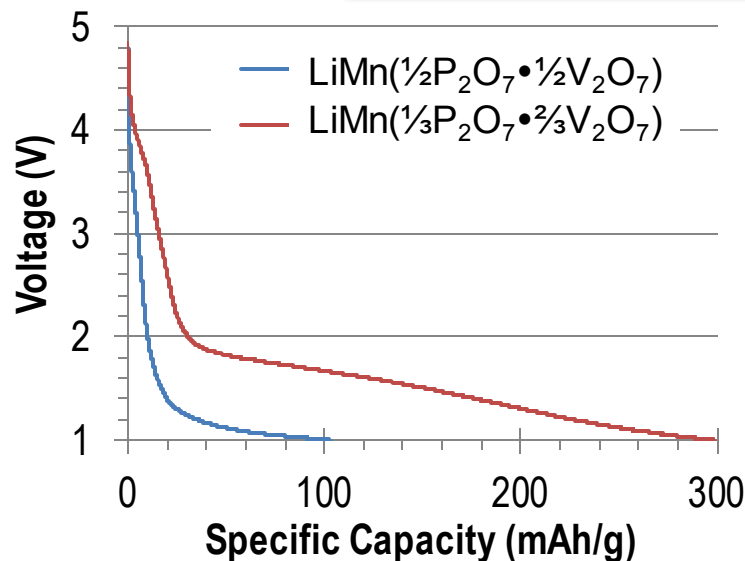
 NORTHWESTERN UNIVERSITY	Valence	Predicted Voltage	Specific Capacity (mAh/g)	Energy density (mWh/g)
$\text{Cu}_3(\text{PO}_4)_2$	Cu^{2+}	3.31 V	380	1258
$\text{Cu}_2(\text{P}_2\text{O}_7)$	Cu^{2+}	3.21 V	326	1045
$\text{Cu}_3(\text{VO}_4)_2$	Cu^{2+}	2.97 V	347	1030
$\text{Cu}_2(\text{PO}_4)$	$\text{Cu}^{2+/1+}$	3.3 V	331	1079
$\text{Fe}(\text{PO}_4)$	Fe^{3+}	2.53 V	468	1183
$\text{Fe}(\text{VO}_4)$	Fe^{3+}	2.40 V	419	1007
$\text{Fe}(\text{PO}_3)_2$	Fe^{2+}	2.19 V	235	514
$\text{Fe}_3(\text{PO}_4)_2$	Fe^{2+}	2.16 V	402	867
$\text{Mn}(\text{PO}_4)$	Mn^{3+}	2.36 V	470	1109
$\text{Mn}(\text{PO}_3)_2$	Mn^{2+}	1.79 V	236	423
$\text{Mn}_3(\text{PO}_4)_2$	Mn^{2+}	1.68 V	405	680
$\text{Mn}_2(\text{P}_2\text{O}_7)$	Mn^{2+}	1.48 V	344	509

- Dr. Wolverton's research group at Northwestern University modeled the theoretical conversion reaction voltages of 100s of crystalline polyanion materials to approximate the discharge voltages of glass-state conversion reactions.
- Experimentally observed voltages in glasses are consistently at least 0.5V lower than modeled values.
- GITT tests underway to measure equilibrium voltages.

Glass cathodes created for multi-valent transitions

- Mn- and Cu-bearing mixed polyanion glasses have been produced with the intent of a multi-valent transition:
Ex: Manganese phosphate vanadate glass can theoretically undergo two valence changes during discharge.

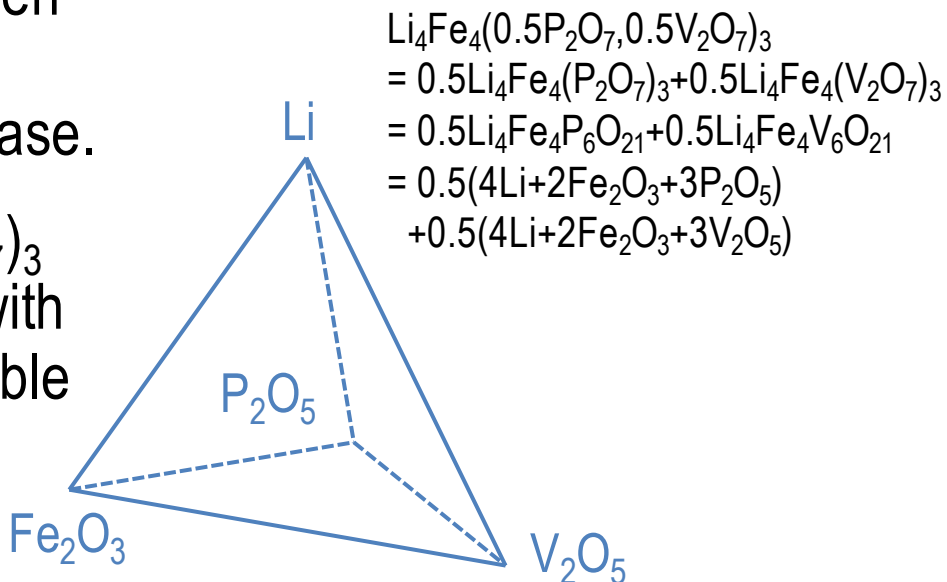
$\text{Mn}(\frac{1}{2}\text{P}_2\text{O}_7 \cdot \frac{1}{2}\text{V}_2\text{O}_7)$	Mn^{4+}
$\text{LiMn}(\frac{1}{2}\text{P}_2\text{O}_7 \cdot \frac{1}{2}\text{V}_2\text{O}_7)$	Mn^{3+}
$\text{Li}_2\text{Mn}(\frac{1}{2}\text{P}_2\text{O}_7 \cdot \frac{1}{2}\text{V}_2\text{O}_7)$	Mn^{2+}
- The intercalation capacity has been far less than expected for even a single valence change.
- Intercalation capacity of Cu-bearing glass has been shown to be temperature dependent, which suggests the capacity is limited by a thermally activated process.



Thermodynamic modeling of $\text{Li}_4\text{Fe}_4(\text{P}_2\text{O}_7 \cdot \text{V}_2\text{O}_7)_3$ glass

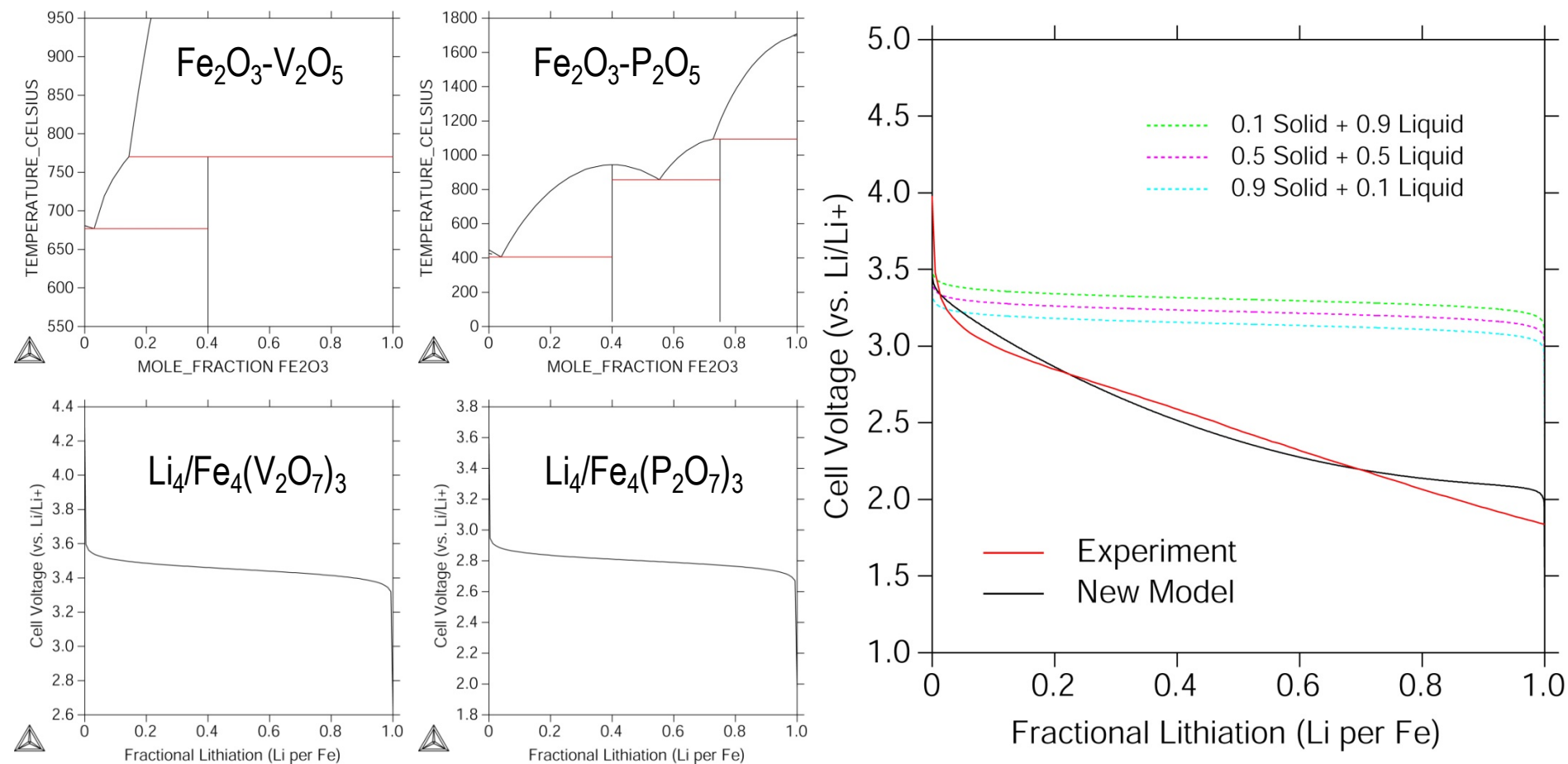
- Thermodynamic descriptions for constituents in $\text{Li}_4\text{Fe}_4((1-x)\text{P}_2\text{O}_7 \cdot x\text{V}_2\text{O}_7)_3$ have been evaluated with pseudo-binary phase diagram and experimental Open Circuit Voltage (OCV) data.
- Thermodynamic model parameters for binary solid and liquid phases have been taken from the Scientific Group Thermodata Europe Substance Database.
- Gibbs energy of hypothetical $\text{Fe}_4(\text{V}_2\text{O}_7)_3$ has been self-consistently evaluated with first-principles calculations of other stable phases in Fe_2O_3 - V_2O_5 pseudo binary.

Thermodynamic modeling of mixed polyanion glass from the evaluated Gibbs energies of crystalline and liquid phases of constituents



New thermodynamic model shows good agreement with experimental data

Technical
Accomplishments



- The new model includes interaction parameters to describe non-ideal mixing between Li^+ and vacancy.

Northwestern collaboration to model glass-state conversion reaction voltages

- Dr. Wolverton's group at Northwestern University has used their Open Quantum Materials Database to predict glass-state conversion voltages.
- Voltages for hundreds of polyanionic materials were calculated.
- Provides guidance for best high energy candidate glasses using glass-state conversion reaction.

	Predicted Voltage	Specific Capacity (mAh/g)	Energy density (mWh/g)
$\text{Ir}(\text{PO}_3)_3$	3.9 V	178	694
$\text{Pd}(\text{PO}_3)_2$	3.9 V	192	744
$\text{Ru}(\text{PO}_3)_3$	3.7 V	224	831
$\text{Pd}(\text{P}_2\text{O}_7)$	3.6 V	258	935
$\text{Ag}_3(\text{PO}_4)$	3.5 V	182	645
$\text{Hg}_3(\text{PO}_4)$	3.5 V	112	396
$\text{Rh}(\text{PO}_4)$	3.4 V	367	1244
$\text{Hg}_2(\text{P}_2\text{O}_7)$	3.4 V	177	599
$\text{Cu}_3(\text{PO}_4)_2$	3.3 V	380	1258
$\text{Cu}_2(\text{PO}_4)$	3.3 V	331	1079



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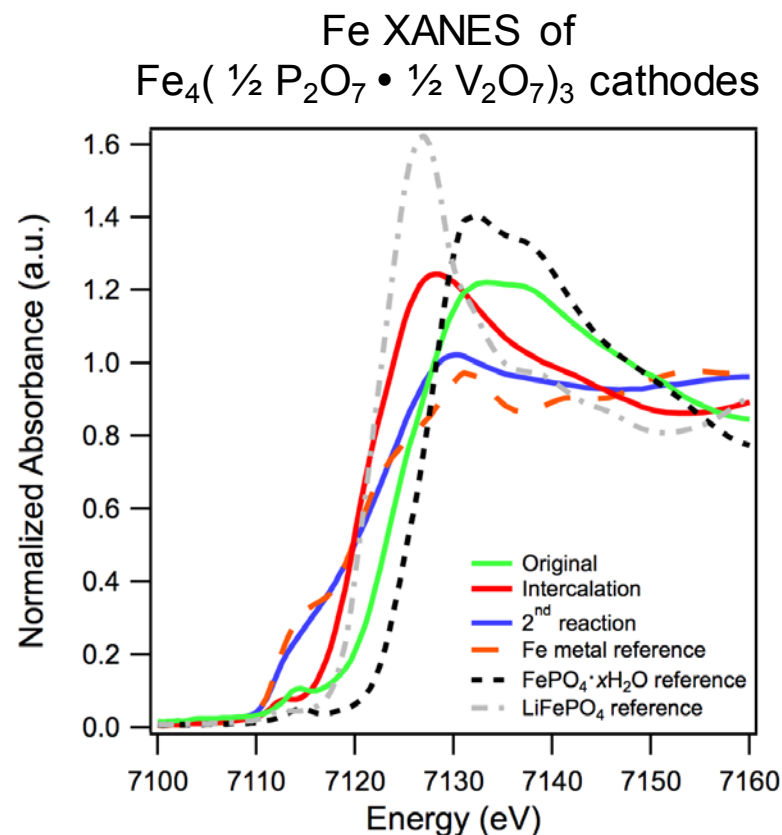
Open university collaboration

- outside the VT program
- no cost

MIT collaboration tracking valence changes of electrochemical reactions

Collaborations

- Dr. Kyler Carroll of MIT led the effort to measure transition metal valence states of glass cathodes at different states of charge using x-ray absorption spectroscopy.
- Experimental work performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.
- Provided first evidence of a glass-state conversion reaction in our cathodes.
- Additional work at NSLS this summer



Collaboration with university

- outside the VT program
- small subcontract to cover travel and work at National Synchrotron Light Source



Remaining challenges and barriers

- Recent preliminary electrochemical impedance spectroscopy experiments have suggested that mixed polyanion glass cathodes may be primarily limited by insufficient ionic diffusivity rather than electrical conductivity.
- Intercalation reactions in non-iron glasses have not approached high specific capacity.
- Glass-state conversion reactions have exhibited a large hysteresis and limited cycleability.

Future work: remainder of FY2014

- Measuring the electrical conductivities of a series of mixed polyanion glasses as a function of polyanionic substitution
- Synthesize, characterize, and perform electrical testing on at least 4 different glass cathode compositions with theoretical specific energies exceeding LiFePO_4 .
 - Have completed:
 - $\text{LiMn}(\frac{1}{2} \text{P}_2\text{O}_7 \bullet \frac{1}{2} \text{V}_2\text{O}_7)$ *>800 mWh/g theoretical*
 - $\text{LiCu}(\frac{1}{2} \text{PO}_3 \bullet \frac{1}{2} \text{VO}_3)_3$ *>600 mWh/g theoretical*
- Perform galvanostatic intermittent titration technique (GITT) testing on mixed polyanion glass cathodes to determine near-equilibrium voltages of glass-state conversion reactions.

- Dec. 2014: Perform electron microscopy on mixed polyanion cathodes at key states of charge.
- Mar. 2015: Produce and electrochemically test mixed polyanion glasses designed to have enhanced ionic diffusivity.
- June 2015: Produce and electrochemically test a mixed polyanion glass designed to have enhanced ionic diffusivity and theoretically capable of a multi-valent intercalation reaction.
- Sept. 2015: Determine the polyanion substitution effect on a series of non-phosphate glasses (go / no go)

Summary

- Mixed polyanion glasses have the potential to overcome the shortcomings in theoretically highly promising crystalline polyanion cathode materials.
- An unexpected high capacity electrochemical reaction has been found in mixed polyanion glass cathodes. X-ray adsorption spectroscopy data has suggested a glass-state conversion reaction mechanism.
- Intercalation reactions in $\text{Fe}_4(\frac{1}{2} \text{P}_2\text{O}_7 \bullet \frac{1}{2} \text{V}_2\text{O}_7)_3$ glass cathodes have shown good cycleability, but glass-state conversion reactions showed substantial capacity fade upon cycling.
- To date, intercalation reactions in Cu- and Mn-based glass cathodes have been limited, but these cathodes demonstrate high capacity glass-state conversion reactions.
- Particle size reduction has been shown to improve the intercalative capacity of mixed polyanion glass cathodes at high discharge rates.
- Thermodynamic modeling at Northwestern Univ. has been used to estimate the discharge voltages of hundreds of glass-state conversion reactions.

Response to FY13 AMR comment:

“This reviewer is unsure if there is any evidence of collaboration outside of ORNL so far.”

- Collaborations outside of ORNL in FY2014 have provided key insights into electrochemical reactions of glass cathodes.
- X-ray absorption spectroscopy with Dr. Kyler Carroll (MIT) was used to study electrochemical reaction mechanisms in glass cathodes and provided key evidence for a glass-state conversion reaction. Dr. Carroll and Dr. Kercher have obtained additional beamtime at Brookhaven National Laboratory this summer to study glass-state conversion reactions in other glass cathodes.
- Computational modeling by Dr. Chris Wolverton (Northwestern) using the Open Quantum Materials Database (OQMD) was used to predict the equilibrium electrochemical potential of hundreds of prospective polyanion glasses based on thermodynamic data of crystalline polyanionic materials.

Response to FY13 AMR comment:

“According to the reviewer, future work should focus on validating that the glassy phase has improved electronic conductivity.”

- The project milestone for June 2014 is the demonstration of electrical conductivity changes due to polyanionic substitution in glass cathode materials.
- Work is on-schedule to meet this milestone.

Response to FY13 AMR comment:

“Conventional LiFePO_4 has terrible conductivity, which is overcome by small (nano) particle size and carbon coating. The reviewer was unsure if the PI can do the same, and if so, does the glass have any advantage.”

- Fine milling of iron pyrophosphate pyrovanadate glass powders was used to increase the powder surface area from 4 m²/g to 25 m²/g (estimated particle size of 100 nm).
- Cathodes of the fine glass powder showed noticeably improved performance at high current, as expected.
- Conventional carbon coating of glass powders cannot be done without crystallizing the glass (measured crystallization temperature ranges from 524°C to 658°C). If carbon coating is needed, other methods will be developed.